at 36 ± 1 °C as previously described.[2] The sulfonic acids were all in the acid form dissolved in deionized water with no added counterion or buffer. All reported chemical shifts are the average of at least two determinations. Sulfonic acids **1a–c** were obtained commercially.

***p*-Nitrobenzenesulfonic Acid.** A solution of *p*-nitrobenzenesulfonyl peroxide[15] (2.0 g, 5 mmol) in chloroform (150 mL) was stirred at room temperature for 1 week. Iodometric titration was used to monitor the disappearance of the peroxide. A white precipitate of *p*-nitrobenzenesulfonic acid [1.46 g (72%)] was removed by filtration and recrystallized from diethyl ether–benzene; mp 108–110 °C. A sample of the acid was converted to the *S*-benzylisothiuronium derivative, mp 199–200 °C (lit.[16] mp 200–202 °C).

***m*-Nitrobenzenesulfonic Acid.** A solution of *m*-nitrobenzenesulfonyl peroxide[15] (0.82 g, 2 mmol) in chloroform (40 mL) was stirred at room temperature for 1 week. The resulting yellow solution was extracted with water (3 × 25 mL), and the water was removed under vacuum. The resulting gray crystals [0.78 g (95%)] were recrystallized from ether–benzene; mp 67–70 °C. A sample of the acid was converted to the *S*-benzylisothiuronium derivative, mp 145–146 °C (lit.[15] mp 145–146 °C).

***p*-Bromobenzenesulfonic Acid.** A solution of *p*-bromobenzenesulfonyl peroxide (1.2 g, 2.5 mmol)[17] in chloroform (100 mL) was stirred for 3 days at room temperature. The orange solution was extracted with water (3 × 25 mL), and the water was removed in vacuo. The resulting yellow crystals [0.9 g (76%)] were recrystallized from ether–benzene; mp 89–90 °C (lit.[18] mp 88 °C).

***m*-(Trifluoromethyl)benzenesulfonic Acid.** A solution of *m*-(trifluoromethyl)benzenesulfonyl peroxide[19] (4 g, 9 mmol) in chloroform was stirred at room temperature for 3 weeks. The acid formed a second layer that was separated from the chloroform solution, dissolved in water, and filtered. The water was removed in vacuo to give white crystals: 1.5 g (37%); mp 42–44 °C. A sample of the acid was converted to the *S*-benzylisothiuronium derivative, mp 137–138 °C (lit.[19] mp 138–139 °C).

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Registry No. $PhSO_3H$, 98-11-3; Me-*m*-$C_6H_4SO_3H$, 617-97-0; Me-*p*-$C_6H_4SO_3H$, 104-15-4; Br-*p*-$C_6H_4SO_3H$, 138-36-3; F_3C-*m*-$C_6H_4SO_3H$, 1643-69-2; O_2N-*m*-$C_6H_4SO_3H$, 98-47-5; O_2N-*p*-$C_6H_4SO_3H$, 138-42-1; Me-*m*-$C_6H_4SO_3^-$, 104994-83-4; Me-*p*-$C_6H_4SO_3^-$, 16722-51-3; Br-*p*-$C_6H_4SO_3^-$, 45900-71-8; F_3C-*m*-$C_6H_4SO_3^-$, 104994-84-5; O_2N-*m*-$C_6H_4SO_3^-$, 30904-40-6; O_2N-*p*-$C_6H_4SO_3^-$, 30904-42-8.

---

[15] Dannley, R. L.; Corbett, G. E. *J. Org. Chem.* **1966**, *31*, 153.

[16] Dannley, R. L.; Hoffman, R. V. *J. Org. Chem.* **1975**, *40*, 2426.

[17] Bolte, J.; Kergomard, A.; Vincent, S. *Tetrahedron Lett.* **1965**, 1529.

[18] Garrick, A. *Z. Chem.* **1869**, 549.

[19] Dannley, R. L.; Tornstrom, P. K. *J. Org. Chem.* **1975**, *40*, 2278.

Experimental Method for the Determination of Cation Binding Constants in Methanol Using Ion-Selective Electrode Methods

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The high level of interest in podands,[1] crown ethers,[2] lariat ethers,[3] cryptands,[4] cavitands,[5] and related species is apparent from the extensive literature in this field that has appeared during the past few years. An important reason for the extensive synthetic effort[6] witnessed recently is the ability of these species to complex cations and molecules. The syntheses of cation binders were followed almost immediately by methods for measuring the cation binding affinities of the various species.

In the earliest work in this area, cation binding affinities were assessed by extraction methods. In these experiments, the salt of a colored organic acid (like picric acid[7]) is dissolved in water and an immiscible organic solvent ($CHCl_3$, CH_2Cl_2) is added. When the two phases are shaken, no extraction occurs because the salt is insoluble in the organic phase. When a lipophilic cation binder is added, the cation is complexed and conducted into the organic phase. The colored anion follows, and the extent of extraction can be assessed colorimetrically or by atomic absorption. Such methods are certainly reliable, but several variables must be controlled in each individual experiment. For example, the same solvent pair, ionic strengths, salt concentrations, temperatures, solvent volumes, etc., must all be kept identical for results to be directly comparable. An example of the problem is found in recent papers by several prominent workers in this field: the solvent systems used have been chloroform–water,[8,9] dichloromethane–water,[10] 1,2-dichloroethane–water,[11] and *o*-dichlorobenzene–butanol.[12]

The extensive work and compilations of Izatt, Christensen, and their co-workers[13] have made homogeneous cation binding constants of considerable value. Frensdorff[14] reported an important method for assessing homogeneous cation binding affinities more than 15 years ago, and this method has been the mainstay of our own group. Following a number of inquiries concerning the experimental details of our method for measuring cation binding affinities using the Frensdorff approach, we set forth this information here.

Experimental Section

Reagents. Reagent-grade methanol was distilled from magnesium turnings through a 20-cm Vigreux column. Either ClO_4^- or Cl^- salts were used. $NaClO_4$, $KClO_4$, NaCl, and KCl were the purest available from Aldrich Chemical Co., recrystallized from water, and dried in a vacuum oven [60 °C (0.05 torr)] for 2 days. NH_4Cl was used as received from Aldrich.

Apparatus. Potentials to within ±0.1 mV were measured on an Orion Model 701A voltmeter. Sodium activity was determined by a sodium ion selective electrode (ISE, Corning Model No.

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[1] Voegtle, F.; Weber, E. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 753.

[2] Voegtle, F.; Weber, E. *Host Guest Complex Chemistry*; Springer Verlag: Weinheim, 1985.

[3] (a) Dishong, D. M; Diamond, C. J.; Cinoman, M. I.; Gokel, G. W. *J. Am. Chem. Soc.* **1983**, *105*, 586. (b) Schultz, R. A.; White, B. D.; Dishong, D. M.; Arnold, K. A.; Gokel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6659.

[4] Lehn, J.-M. *Science (Washington, D.C.)* **1985**, *227*, 849.

[5] (a) Cram, D. J. *Science (Washington, D.C.)* **1983**, *219*, 1177. (b) Cram, D. J.; Trueblood, K. N. In *Host Guest Complex Chemistry: Macrocycles*; Voegtle, F., Weber, E., Eds.; Springer Verlag: Weinheim, 1985; pp 125–188.

[6] Gokel, G. W.; Korzeniowski, S. H. *Macrocyclic Polyether Syntheses*; Springer Verlag: Weinheim, 1982.

[7] Pedersen, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

[8] Strzelbicki, J.; Bartsch, R. A. *Anal. Chem.* **1981**, *53*, 1894.

[9] Pacey, G. E.; Wu, Y. P.; Bubnis, B. P. *Analyst* **1981**, *106*, 636.

[10] Kawakami, Y.; Sugiura, T.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3053.

[11] Bartsch, R. A.; Czech, B. P.; Kang, S. I.; Stewart, L. E.; Walkowiak, W.; Charewicz, W. A.; Heo, G. S.; Son, B. *J. Am. Chem. Soc.* **1985**, *107*, 4997.

[12] (a) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111. (b) Shinkai, S.; Minami, T.; Kusano, Y.; Manabe, O.; *Tetrahedron Lett.* **1982**, 2584.

[13] Izatt, R. M.; Bradshaw, J. S.; Nielson, S. A.; Lamb, J. D.; Christensen, J. J. *Chem. Rev.* **1985**, *85*, 271.

[14] Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.

0022-3263/86/1951-5015$01.50/0

476210). Potassium and ammonium cation activities were determined by a Corning monovalent cation electrode, Model No. 476220. A Corning Ag/AgCl reference electrode (Model 476029) was used with each of the ion-selective electrodes. A water bath, placed on a magnetic stirrer, was maintained at 25 ± 0.2 °C with a Cole Parmer circulator heater (Model 125200). Sample cells were constructed from 50-mL rimless beakers (50-mm height by 41-mm diameter) capped by a Teflon top (50 mm diameter, tapered to fit) drilled with three holes. Two holes were drilled to accommodate the electrodes (each approximately 12 mm), and a third hole approximately 8 mm was drilled to accommodate a digital thermocouple inserted in the sample cell to monitor temperature.

Procedure. New electrodes were conditioned in 1 M salt solutions stepwise to 100% MeOH over a 10-day period, starting with 1 M salt in 90% H_2O-10% MeOH solution. The MeOH was increased by 10% per day while the H_2O was decreased by 10%. The salt concentration was kept constant at 1 M. NaCl was used to condition the Na^+ ISE, and KCl was used for the monovalent ISE. Once at 100% MeOH, the electrodes were thereafter kept in a 4 mM salt solution. Each ion-selective electrode was tested as described in its manual for Nernstian response.

A 2.000 mM stock salt solution (50 mL) and a 5.000 mM (25 mL) stock crown solution were prepared. A 1.000 mM salt reference sample was prepared in a sample cell by pipetting 10 mL of stock salt solution and 10 mL of MeOH. Three crown plus salt samples were prepared as follows: 10 mL of salt + 10 mL of crown, 10 mL of salt + 8 mL of crown + 2 mL of MeOH, and 10 mL of salt + 6 mL of crown + 4 mL of MeOH. The samples were 2.500, 2.000, and 1.500 mM with respect to crown. The potential of the reference sample was measured at 25 °C by taking readings at 5-min intervals until three successive readings differed by 0.2 mV or less. The solution was stirred except while recording a voltage. Potentials of the crown and salt samples were determined in the same manner. At least two trials of all samples were measured.

Calculations. The stability constant for a 1:1 crown–metal complex is defined as

$$K_S = [MCr^+]/[M^+][Cr]$$

assuming activity coefficients of 1. The concentration of free $[M^+]$ was calculated at 25 °C by the Nernst equation as follows:

$$\Delta E = E_{ref}\ (V) - E_{crown}\ (V) \qquad (1)$$

$$[M^+]_{free} = e^{-\Delta EnF/RT}[M^+]_{ref}$$

$$[M^+]_{free} = 10^{-\Delta E/0.0591}[M^+]_{ref} \qquad (2)$$

The complex concentration is calculated by subtracting $[M^+]_{free}$ from the total salt concentration added to the sample. In the samples described the total salt concentration was 0.001 000 M.

$$[MCr^+] = [M^+]_{total} - [M^+]_{free}$$

$$[MCr^+] = 0.001\,000 - [M^+]_{free} \qquad (3)$$

From the total crown concentration and the complex concentration, $[Cr]_{free}$ was calculated. In the samples described the total crown concentrations were 0.002 500, 0.002 000, and 0.001 500 M.

$$[Cr]_{free} = [Cr]_{total} - [MCr^+] \qquad (4)$$

The equilibrium constant, K_S, is calculated from the values of $[M^+]_{free}$, $[Cr]_{free}$, and $[MCr^+]$. The log K_S values of all the trials were averaged. If the standard deviation was more than +0.04 log unit, then the experiment was repeated. If the values still had a standard deviation >0.04, the situation is probably complicated by the presence of second-order or higher equilibria. In such a case, the titration method and calculations described by Frensdorff[14] were used.

Discussion

When we first began routinely determining cation binding constants, the experiment was done in a glovebox using a di-*n*-butyl phthalate bath for temperature control. After much study, we found that the results are the same in a water bath open to the atmosphere. If the electrodes give less than a Nernstian slope, it generally means the membrane is clogged. Sodium ion selective electrode membranes can be cleaned with pumice as described in the instruction manual. We have found that both the sodium and monovalent cation electrodes can be cleaned by sonicating them in a 4 mM salt solution for 15 min. The minimum lifetime of properly handled electrodes is 6 months, but our electrodes have usually remained serviceable for periods up to 18 months. Stability constants of 18-crown-6 in MeOH measured in our laboratory[15] using this procedure are log $K_S(Na^+) = 4.35$ and log $K_S(K^+) = 6.08$. Literature values obtained calorimetrically[16] and spectrophotometrically[17] are log $K_S(Na^+) = 4.36$, 4.32 and log $K_S(K^+) = 6.06$, 6.10, respectively. These values are within experimental error of our values validating the procedure.

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Registry No. MeOH, 67-56-1; 18-crown-6·Na^+, 31270-12-9; 18-crown-6·K^+, 31270-13-0.

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(15) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786.

(16) Haymore, B. L.; Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Inorg. Chem.* **1982**, *21*, 1598.

(17) Ikeda, I.; Emura, H.; Yamamura, S.; Okahara, M. *J. Org. Chem.* **1982**, *47*, 5150.

Determination of Solvolysis Products from 1-Substituted Tetracyclodecanes by 2D-NMR and Molecular Mechanics

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In a previous paper[1] we reported the kinetic results of the solvolysis of some 1-substituted tetracyclononanes and tetracyclodecanes. This study included the acetolysis of *trans*-(tetracyclo[3.3.2.$0^{2,4}$.$0^{6,8}$]dec-1-yl)methyl tosylate (**1**) and *endo,exo*-(tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]non-1-yl)methyl tosylate (**2**). It was concluded that adding a second cyclopropane ring did not substantially increase the amount of participation by the corner of a cyclopropane ring compared to similar tricyclic systems with only one cyclopropane ring analogously situated,[2,3] as shown by the similarity in solvolytic rates.

During this study an interesting and challenging problem developed in attempting to determine the structure of the solvolysis products of tosylates such as **1** and **2**.

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(1) Chenier, P. J.; Christie, D. M., Goettl, V. M. *J. Org. Chem.* **1985**, *50*, 3213.

(2) Chenier, P. J.; Kiland, P. J.; Schmitt, G. D.; Vander Wegen, P. G. *J. Org. Chem.* **1980**, *45*, 5413.

(3) Chenier, P. J.; Jenson, T. M.; Wulff, W. D. *J. Org. Chem.* **1982**, *47*, 770.

0022-3263/86/1951-5016$01.50/0